Tuning the Thermotropic and Lyotropic Properties of Liquid-Crystalline Terpyridine Ligands

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Experimental section:

The 300 and 200 (1H), 75.47 (13C) MHz NMR spectra were recorded at room temperature with perdeuterated solvents with residual protiated solvent signals providing internal references.

Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 instrument. The samples were examined at a scanning rate of 10 K.min⁻¹ by applying two heating and one cooling cycle. The apparatus was calibrated with indium (156.6 °C) and gallium (29.8 °C). ThermoGravimetric Analyses (TGA) were performed on SDTQ 600 apparatus at scanning rate of 10 K.min⁻¹ under argon.

Phase behaviour was studied by polarized light optical microscopy (POM) on a Leitz microscope equipped with a Mettler-Toledo FP80 hot-stage and an FP80 central processor.

X-ray scattering measurements were carried out with two different experimental set-ups. In both cases, a linear monochromatic Cu-Kα1 beam (\( \lambda = 1.5405 \) Å) was obtained using a sealed-tube generator (900W) equipped with a bent monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like geometry was used in the second experimental set-up. In all cases, the crude powder was filled in Lindemann glass capillaries of 1 mm diameter and 10 µm wall thickness. An initial set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured and the sample temperature controlled to within ± 0.05 °C. The second set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature controlled to within ± 0.3 °C. In each case, exposure times were varied from 1 to 48 h. \( d_{calc} \) is deduced from the following mathematical expression:

\[
\langle d_{001} \rangle = \frac{1}{N_l} \sum d_{001,l} \text{where } N_l \text{ is the number of } 00l \text{ reflections for the lamellar phase.}
\]

The molecular volume \( V_m \) is defined by

\[
V_m = \frac{M}{0.6022 \ V_{ch}(T)}
\]

with \( M \) the molecular weight and \( V_{ch}(T) = 26.5616 + 0.02023T \) (\( T \) in °C, \( T_0 = 25 \) °C) (For T\textsuperscript{12}ester: \( V_m = 3200 \) Å\(^3\) at 100 °C and \( V_m = 3350 \) Å\(^3\) at 180 °C; For T\textsuperscript{12}amide: \( V_m = 3200 \) Å\(^3\) at 120 °C; For T\textsuperscript{12}ethynyl: \( V_m = 3200 \) Å\(^3\) at 198 °C).

Small-angle X-ray scattering experiments with gel samples were performed with laboratory setups already described in detail.\([S1],[S2]\) The X-rays delivered by a rotating-anode generator were focused and monochromatized (\( \lambda_{CuK\alpha} = 1.541 \) Å) either by a curved graphite
monochromator or by a set of two perpendicular curved nickel-coated mirrors. Samples were held in cylindrical Lindemann glass capillaries of 1 mm diameter and 10 µm wall thickness. Vacuum flight tubes were used to decrease adsorption and parasitic scattering by the air. The scattered X-rays were detected with imaging plates and the sample-detection distance varied from 20 to 60 cm, depending on the scattering angles of the signals. The q-range explored ranged from 0.02 to 0.6 Å\(^{-1}\) where q is the scattering vector modulus q = \((4\pi/\lambda)\sin\theta\) and 2\(\theta\) is the scattering angle. Exposure times varied from 1 to 20 hours depending on which setup was used and on the strength of the scattering signal.

UV-vis spectra were recorded using a UVIKON 940/941 dual-beam grating spectrophotometer (Kontron Instruments) with a 1 cm quartz cell.

FT-IR spectra were recorded using a Perkin-Elmer “spectrum one” spectrometer on the neat liquids or as thin films, prepared with a drop of dichloromethane and evaporated to dryness on KBr pellets.

The molecular modeling calculations were performed on an SGI Origin 200 4 CPU computer and on an SGI Octane² workstation using the DISCOVER 3 molecular mechanics package from Accelrys (www.accelrys.com) with the pcff force field.

For classical transmission electron microscopy on diluted solution, a 5µl drop of the solution at 0.04 %w/w is deposited onto a carbon coated grid, after 1 min adsorption the excess of liquid is wiped out with a piece of filter paper and the grid is air dried and further rotary shadowed with W/Pt. Freeze fracture electron microscopy (FFEM) on gels was performed as follow: a small piece of gel is placed between two copper holders and rapidly plunged in liquid nitrogen, due to the speed of freezing the solvent stays in an amorphous state enabling the preservation of the fine inner structure of the gel. The holder is then transferred under liquid nitrogen in a cryo fracture apparatus developed by Dr. J.-C. Homo and maintained at –160 °C and a vacuum around 10\(^{-8}\) mbar. The sample is fractured and immediately shadowed with a layer of 2 nm of Pt under an angle of 45°. A thick layer of carbon at 90° reinforces the replicas (around 20 nm). Finally the latter are carefully washed and transferred onto a grid for further observation in the microscope (CM12 Philips).

**Synthetic procedures:**
Ethyl-4-methyl-3,5-diaminobenzoate\(^{[3]}\) and 3,4,5 trialkyloxybenzoic chloride with C\(_8\), C\(_{12}\) and C\(_{16}\) chains\(^{[4]}\) were synthesized as previously reported.
**Ethyl-3,5-bis(3,4,5-trioctyloxybenzoylamino)-4-methyl benzoate.**

150 mL of dry acetone containing 500 mg of Ethyl-4-methyl-3,5-diaminobenzoate (2.8 mmol), 3.68 g of 3,4,5 trioctyloxybenzoic chloride (7 mmol) and 1.48 g anhydrous Na$_2$CO$_3$ (14 mmol) was refluxed during 12 hours under argon. Na$_2$CO$_3$ excess was filtered out hot and diamine was precipitate in acetone at low temperature (-20 °C). Purification was performed by crystallisation in hot acetone solution to afford 2.7 g of pure compound (82 %). $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 0.88 (m, 18H, CH$_3$), 1.29 (m, 63H, CH$_2$ + CH$_3$ ester), 1.775 (m, 12 H, CH$_2$), 2.15 (s, 3H, CH$_3$), 4.03 (t, $^4$J = 5.8 Hz, 12H, OCH$_2$), 4.29 (q, $^4$J = 7.3 Hz, 2H, CH$_2$ ester), 7.14 (s, 4H, H arom.), 8.00 (s, 2H, H arom.), 8.05 (s, 2H, NH). $^{13}$C{$^1$H} DEPT NMR (75.47 MHz, CDCl$_3$) 13.82 (CH$_3$), 14.07 (CH$_3$), 14.19 (CH$_3$), 22.66 (CH$_2$), 26.11(CH$_2$), 29.29 (CH$_2$), 29.38 (CH$_2$), 29.54 (CH$_2$), 29.80 (CH$_2$), 30.36 (CH$_2$), 31.83 (CH$_2$), 31.90 (CH$_2$), 32.01 (CH$_2$), 61.14 (OCH$_2$), 69.40 (OCH$_2$), 73.56 (OCH$_2$), 106.09 (CH), 123.85 (CH), 128.74 (Cq), 133.00 (Cq), 135.76 (Cq), 141.79 (Cq), 152.21 (Cq), 153.28 (Cq), 165.74 (C=O), 166.09 (C=O). UV-vis (CH$_2$Cl$_2$, 23 °C) : $\lambda_{max}$ ($\epsilon$, M$^{-1}$cm$^{-1}$) = 272 (49600). IR (KBr) : 3438 (vNH), 3267 (vNH), 2925, 2855, 1720 (vCOO), 1639 (vCO), 1581, 1520 (\(\delta\)NH), 1489, 1468, 1384, 1336, 1215, 1113 cm$^{-1}$. MS (FAB+, mNBA): m/z (%) = 1171.2 (100) [M+H]$^+$, 1057.2 (20) [M-C$_8$H$_{17}$]$^+$. Anal. Calcd for C$_{72}$H$_{118}$N$_2$O$_{10}$: C, 73.80; H, 10.15; N, 2.39; Found C, 73.65; H, 9.88; N, 2.13.

**Ethyl-3,5-bis(3,4,5-tridodecyloxybenzoylamino)-4-methyl benzoate.**

To a solution of Ethyl-4-methyl-3,5-diaminobenzoate (1.27 g, 7.1 mmol) in 250 mL of dry acetone was added 2.5 equivalents of 3,4,5 tridodecyloxybenzoic chloride (12.34 g, 17.8 mmol) and 5 equivalents of anhydrous Na$_2$CO$_3$ (3.76 g, 35.5 mmol). The mixture was stirred under reflux for 20 hours. The white precipitate obtained after cooling to room temperature was filtered and washed with water in order to remove the unreacted Na$_2$CO$_3$. The pure product was obtained by double crystallisation in hot acetone and in a CH$_2$Cl$_2$/CH$_3$CN mixture (8.1 g, 82%). $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 0.88 (m, 18H, CH$_3$), 1.26 (m, 111H, CH$_2$ + CH$_3$ ester), 1.79 (m, 12 H, CH$_2$), 2.24 (s, 3H, CH$_3$), 4.02 (m, 12H, OCH$_2$), 4.34 (q, $^4$J = 7.0 Hz, 2H, CH$_2$ ester), 7.11 (s, 4H, H arom.), 7.80 (s, 2H, H arom.), 8.12 (s, 2H, NH). $^{13}$C{$^1$H} DEPT NMR (75.47 MHz, CDCl$_3$) 13.83 (CH$_3$), 14.08 (CH$_3$), 14.08 (CH$_3$), 22.68 (CH$_2$), 26.13 (CH$_2$), 29.37 (CH$_2$), 29.40 (CH$_2$), 29.45 (CH$_2$), 29.54 (CH$_2$), 29.67 (CH$_2$), 29.72 (CH$_2$), 29.76 (CH$_2$), 30.01 (CH$_2$), 30.37 (CH$_2$), 31.93 (CH$_2$), 32.03 (CH$_2$), 61.16 (OCH$_2$), 69.43 (OCH$_2$), 73.57 (OCH$_2$), 106.07 (CH), 123.81 (CH), 128.78 (Cq), 132.81 (Cq), 136.49 (Cq), 141.82
Ethyl-3,5-bis(3,4,5-trihexadecyloxybenzoylamino)-4-methyl benzoate.

This compound was prepared from 500 mg of Ethyl-4-methyl-3,5-diaminobenzoate (2.8 mmol), 6.04 g of 3,4,5 trihexadecyloxybenzoic chloride (7 mmol, 2.5 eq.) and 1.48 g anhydrous Na$_2$CO$_3$ (14 mmol, 5 eq.) in 250 mL of dry acetone refluxed during 12 hours under argon. The precipitate was filtered hot. The product was dissolved in hot acetone and Na$_2$CO$_3$ excess was filtered out hot. The white product crystallized at room temperature (2.95 g, 57 %). $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 0.87 (t, $^3J = 6.2$ Hz, 18H, CH$_3$), 1.25 (m, 159 H, CH$_2$ + CH$_3$ ester), 1.78 (m, 12 H, CH$_2$), 2.20 (s, 3H, CH$_3$), 4.04 (t, $^3J = 5.8$ Hz, 12H, OCH$_2$), 4.33 (q, $^3J = 6.9$ Hz, 2H, CH$_2$ ester), 7.12 (s, 4H, H arom.), 7.89 (s, 2H, H arom.), 8.08 (s, 2H, NH). $^{13}$C{$_^1$H} DEPT NMR (75.47 MHz, CDCl$_3$) 13.86 (CH$_3$), 14.09 (CH$_3$), 14.24 (CH$_3$), 22.68 (CH$_2$), 26.13 (CH$_2$), 29.37 (CH$_2$), 29.41 (CH$_2$), 29.46 (CH$_2$), 29.63 (CH$_2$), 29.68 (CH$_2$), 29.73 (CH$_2$), 29.76 (CH$_2$), 30.38 (CH$_2$), 31.93 (CH$_2$), 61.13 (OCH$_2$), 69.44 (OCH$_2$), 73.58 (OCH$_2$), 106.07 (CH), 123.74 (CH), 128.80 (Cq), 132.73 (Cq), 136.51 (Cq), 141.81 (Cq), 152.89 (Cq), 153.30 (Cq), 165.65 (C=O), 166.03 (C=O). UV-vis (CH$_2$Cl$_2$, 23 °C) : $\lambda$max (ε, M$^{-1}$cm$^{-1}$) = 272 (44900). IR (KBr) : 3438 (vNH), 3261 (vNH), 2917, 2850, 1721 (vCOO), 1618 (vCO), 1581, 1520 (δNH), 1489, 1467, 1426, 1384, 1337, 1216, 1116 cm$^{-1}$. MS (FAB+, mNBA): m/z (%) = 1844.2 (100) [M+H]$^+$, 1618.2 (15) [M-C$_{16}$H$_{33}$]$^+$. Anal. Calcd for C$_{120}$H$_{214}$N$_2$O$_{10}$: C, 78.12; H, 11.69 ; N, 1.52; Found C,77.85; H, 11.43; N, 1.35.

3,5-bis(3,4,5-trioctyloxybenzoylamino)-4-methyl benzoic acid.

A mixture of Ethyl-3,5-bis(3,4,5-trioctyloxybenzoylamino)-4-methyl benzoate (1.051 g, 0.9 mmol) and KOH (2.52 g, 45 mmol) in 100 mL THF/H$_2$O (90/10 V/V) was refluxed overnight. After complete consumption of the starting material, the pH of the hot mixture was adjusted to 2 with 10 % V/V dilute HCl solution. After cooling to room temperature, removal of the THF led to the precipitation of the product. The white powder obtained was washed with water and dried (0.87 g, 85 %). Due to the low solubility of 3,5-bis(3,4,5-trioctyloxybenzoylamino)-4-methyl benzoic acid in all common deuterated solvents, even in
the presence of base, NMR experiments could not be performed. But an esterification reaction with H$_2$SO$_4$ in ethanol on this product led to the formation of the starting material Ethyl-3,5-bis(3,4,5-trioctyloxybenzoylamino)-4-methyl benzoate. This result confirms the formation and the integrity of the platform under acid form. UV-vis (CH$_2$Cl$_2$, 23 °C) : $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$) = 272 (55990). IR (KBr) : 3438 (vNH), 3214 (vNH), 2925, 2855, 1691 (vCOO), 1640 (vCO), 1619 (vCO), 1583, 1517 (δNH), 1493, 1467, 1428, 1385, 1336, 1273, 1261, 1115 cm$^{-1}$. MS (FAB+, mNBA): m/z (%) = 1125.2 (60) [M-OH]$^+$. Anal. Calcd for C$_{70}$H$_{114}$N$_2$O$_{10}$$\cdot$H$_2$O: C, 72.37; H, 10.06; N, 2.41; Found C, 72.13; H, 9.70; N, 2.15.

3,5-bis(3,4,5-tridodecyloxybenzoylamino)-4-methyl benzoic acid.

To a stirred solution of Ethyl-3,5-bis(3,4,5-tridodecyloxybenzoylamino)-4-methyl benzoate (0.6 g, 0.4 mmol) in 100 mL THF/H$_2$O (90/10 V/V) was added 50 equivalents of KOH (1.11 g, 20 mmol). The mixture was refluxed 20 hours. The pH of the hot mixture was adjusted to 2 with dilute HCl solution. After cooling to room temperature, removal of the THF led to the precipitation of the product. The white powder obtained was washed with water and dried (0.48 g, 82 %). As mentioned before, due to the low solubility of the product in all common deuterated solvents, NMR experiments could not be performed. A back reaction with H$_2$SO$_4$ in ethanol led to formation of the platform bearing an ester. This result also confirms here the formation and the integrity of the platform under acid form. UV-vis (CH$_2$Cl$_2$, 23 °C) : $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$) = 273 (50700). IR (KBr) : 3437 (vNH), 3246 (vNH), 2920, 2851, 1694 (vCOO), 1642 (vCO), 1618 (vCO), 1583, 1527 (δNH), 1490, 1467, 1428, 1385, 1337, 1275, 1262, 1234, 1214, 1119, 1074, 1044 cm$^{-1}$. MS (FAB+, mNBA): m/z (%) = 1462.2 (70) [M-OH]$^+$. Anal. Calcd for C$_{94}$H$_{162}$N$_2$O$_{10}$$\cdot$H$_2$O: C, 75.35; H, 11.03; N, 1.87; Found C, 75.10; H, 10.82; N, 1.75.

3,5-bis(3,4,5-trihexadecyloxybenzoylamino)-4-methyl benzoic acid.

500 mg of Ethyl-3,5-bis(3,4,5-trihexadecyloxybenzoylamino)-4-methyl benzoate (0.27 mmol) and KOH (0.76 g, 14 mmol) in 50 mL THF/H$_2$O (90/10 V/V) was refluxed overnight. The pH of the hot mixture was adjusted to 2 with 10 % V/V dilute HCl solution and cooling of the solution in a deep freezer led to the precipitation of the product. The white powder obtained was washed with water and dried (0.36 g, 73 %). As stated above, NMR experiments could
not be performed. Esterification of the product with H$_2$SO$_4$ in ethanol also confirms the formation and the integrity of the platform under acid form. UV-vis (CH$_2$Cl$_2$, 23 °C) : $\lambda_{\text{max}}$ (ε, M$^{-1}$ cm$^{-1}$) = 272 (52100). IR (KBr) : 3437 (νNH), 3203 (νNH), 2918, 2850, 1692 (νCOO), 1638 (νCO), 1617 (νCO), 1582, 1512 (δNH), 1486, 1467, 1428, 1385, 1339, 1275, 1256, 1231, 1115, 1072, 1043 cm$^{-1}$. MS (FAB+, m/NBA): $m/z$ (%) = 1816.2 (100) [M+H$^+$], 1770.2 (20) [M-COOH]$^+$. Anal. Calcd for C$_{118}$H$_{210}$N$_2$O$_{10}$•H$_2$O: C, 77.24; H, 11.65; N, 1.53; Found C, 77.02; H, 11.41; N, 1.32.

4′-bromomethyl-2,2′;6′2′′-terpyridine.
4′-bromomethyl-2,2′;6′2′′-terpyridine was synthesized from 4′-methyl-2,2′;6′2′′-terpyridine (0.515 g, 2 mmol) by radical bromination with bromosuccinimide (0.41 g, 2.2 mmol) in presence of 2,2′-azo-bis-isobutyrylnitrile (AIBN) (0.01 g, 0.07 mmol) in 100 mL benzene/H$_2$O (50/50 V/V) mixture under irradiation with a 100 watts halogen lamp during 3 hours and under reflux. The solution was filtered over alumina and dried over MgSO$_4$. After evaporation of the solvent, purification of the product was performed by flash chromatography on silica gel with CH$_2$Cl$_2$/MeOH (99.9/0.1 to 99.5/0.5) (0.17 g, 25%). $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 4.57 (s, 2H, CH$_2$), 7.35 (ddd, $^{3}J = 7.7$ Hz, $^{4}J = 4.8$ Hz, $^{4}J = 1.1$ Hz, 2 H, CH), 7.86 (td, $^{3}J = 7.7$ Hz, $^{4}J = 1.8$, 2 H, CH), 8.49 (s, 2H, CH), 8.61 (d, $^{3}J = 7.7$ Hz, 2H, CH), 8.71 (d, br, $^{3}J = 4.8$ Hz, 2H, CH).

4′-aminomethyl-2,2′;6′2′′-terpyridine.
i) 4′-bromomethyl-2,2′;6′2′′-terpyridine (0.72 g, 2.2 mmol) was refluxed overnight with 1.1 equiv. of hexamethylenetetramine (0.34 g, 2.4 mmol) in 40 mL of CH$_2$Cl$_2$. The precipitate obtained at room temperature was filtered and washed with ether (0.9 g). ii) 0.9 g of this hexamethylenetetrammonium precipitate (1.9 mmol) with bromide as counter-ion was refluxed 3 hours in 30 mL of EtOH with 4.4 mL of concentrated HCl solution. The white precipitate obtained after cooling to room temperature was filtered and washed with ether. The obtained ammonium salt with chloride as counter-ion (0.2 g, 0.6 mmol) was then dispersed in 10 mL of concentrated NaOH solution (10 g of NaOH in 30 mL of water). The product under amino form was extracted several times with CH$_2$Cl$_2$. The dichloromethane solution was dried over MgSO$_4$ and after removal of the solvent, pure 4′-aminomethyl-2,2′;6′2′′-terpyridine was obtained as a yellow powder (0.13 g). The overall yield of the reaction is 60 %. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 1.68 (s, 2H, NH$_2$), 4.04 (s, 2H, CH$_2$), 7.31 (ddd, $^{3}J = 7.5$ Hz, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz, 2 H, CH), 7.84 (td, $^{3}J = 7.8$ Hz, $^{4}J = 1.75$, 2 H,
CH), 8.40 (s, 2H, CH), 8.60 (dt, $^3J = 7.8$ Hz, $^4J = 0.9$ Hz, 2H, CH), 8.69 (ddd, $^3J = 4.8$ Hz, $^3J = 1.75$ Hz, $^4J = 0.9$ Hz, 2H, CH). $^{13}$C{${}^1$H} DEPT NMR (75.47 MHz, CDCl$_3$) 45.90 (CH$_2$), 119.18 (CH), 121.32 (CH), 123.77 (CH), 136.74 (CH), 149.08 (CH), 154.39 (Cq), 155.66 (Cq), 156.23 (Cq). UV-vis (CH$_2$Cl$_2$, 23 °C) : λ$_{\text{max}}$ (ε, M$^{-1}$ cm$^{-1}$) = 281 (30900). IR (KBr) : 3436 (νNH$_2$), 3368 (νNH$_2$), 3056 (νCH), 3013 (νCH), 2924 (νCH), 2854 (νCH), 1605, 1584 (νC=C, νC=N), 1565, 1469, 1407 (νCH$_2$), 1263 (νNH$_2$), 1121, 1090, 1072, 1043, 990, 875 cm$^{-1}$. MS (FAB+, m/NBA): m/z (%) = 263.2 (100) [M+H]$^+$. Anal. Calcd for C$_{16}$H$_{14}$N$_4$•H$_2$O: C, 68.55; H, 5.75; N, 19.99; Found C, 68.34; H, 5.54; N, 19.72.

**T**$^8$ester

3,5-bis(3,4,5-trioctyloxybenzoylamino)-4-methyl benzoic acid (0.500 g, 0.437 mmol) dimethylaminopyridine (DMAP) (0.053 g, 0.437 mmol) were introduced in 20 mL distilled CH$_2$Cl$_2$ in a Schlenck flask under inert atmosphere (argon). The mixture was stirred until complete solubilisation of the acid. Finally 1-[3-(dimethyl-amino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI) (0.084 g, 0.437 mmol) and 4'-hydroxymethyl-2,2';6'2''-terpyridine (0.116 g, 0.437 mmol) were added to the clear solution which was stirred overnight. After evaporation of the solvent, purification was performed by flash chromatography on silica gel with CH$_2$Cl$_2$/MeOH (99/1 to 97/3) and followed by crystallisation from CH$_2$Cl$_2$/CH$_3$CN (0.462 g, 76%). $^1$H NMR (CDCl$_3$, 200 MHz) δ 0.85 (t, $^3J = 4.9$ Hz, 18H, CH$_3$), 1.25 (m, 60 H, CH$_2$), 1.70 (m, 12 H, CH$_2$), 2.08 (s, 3H, CH$_3$), 3.88 (m, 12H, OCH$_2$), 5.37 (s, 2H, OCH$_2$), 7.09 (s, 4H, H arom.), 7.27 (ddd, $^3J = 7.8$ Hz, $^3J = 4.3$ Hz, $^4J = 1.6$ Hz, 2 H, CH), 7.80 (td, $^3J = 7.7$ Hz, $^4J = 1.8$ Hz, 2 H, CH), 8.04 (s, 2H, CH), 8.33 (s, 2H, CH), 8.57 (m, 6H, CH + NH). $^{13}$C{${}^1$H} DEPT NMR (75.47 MHz, CDCl$_3$) 14.03 (CH$_3$), 14.09 (CH$_3$), 22.66 (CH$_2$), 22.70 (CH$_2$), 26.08 (CH$_2$), 29.29 (CH$_2$), 29.34 (CH$_2$), 29.38 (CH$_2$), 29.54 (CH$_2$), 30.34 (CH$_2$), 31.83 (CH$_2$), 31.91 (CH$_2$), 65.22 (OCH$_2$), 69.18 (OCH$_2$), 73.47 (OCH$_2$), 105.96 (CH), 119.16 (CH), 121.45 (CH), 123.92 (CH), 124.42 (CH), 136.85 (CH), 148.93 (CH), 127.73 (Cq), 128.86 (Cq), 134.07 (Cq), 136.87 (Cq), 141.42 (Cq), 146.97 (Cq), 153.08 (Cq), 155.62 (Cq), 155.78 (Cq), 165.20 (C=O), 166.38 (C=O). UV-vis (CH$_2$Cl$_2$, 23 °C) : λ$_{\text{max}}$ (ε, M$^{-1}$ cm$^{-1}$) = 276 (91800), 252 (78800). IR (KBr) : 3437 (vNH), 3232 (vNH), 2924 (vCH), 2853(vCH), 1728 (vCOO), 1637 (vCO), 1618 (vCO), 1584 (vC=C, vC=N), 1517 (δNH), 1488, 1465, 1455, 1426, 1384, 1336, 1275, 1261, 1235, 1214, 1112, 1069, 1041
cm$^{-1}$. MS (FAB+, mNBA): $m/z$ (%) = 1389.2 (100) [M+H]$^+$. Anal. Calcd for C$_{86}$H$_{125}$N$_5$O$_{10}$: C, 74.37; H, 9.07 ; N, 5.04; Found C, 74.08; H, 8.87; N, 4.75.

**T$_{16}$ester**

3,5-bis(3,4,5-trihexdecyloxybenzoylamino)-4-methyl benzoic acid (0.500 g, 0.275 mmol) and dimethylaminopyridine (DMAP) (0.034 g, 0.275 mmol) and were introduced in 20 mL of distilled CH$_2$Cl$_2$ in a Schlenck flask under argon. The mixture was stirred until complete solubilisation of the acid. Finally 1-[3-(dimethyl-amino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI) (0.053 g, 0.275 mmol) and 4'-hydroxymethyl-2,2':6,2''-terpyridine (0.073 g, 0.275 mmol) were added to the clear solution which was stirred overnight. After removal of the solvent, purification of the product was performed by flash chromatography on silica gel with CH$_2$Cl$_2$/MeOH (100/0 to 99/1) and followed by crystallization from CH$_2$Cl$_2$/CH$_3$CN (0.390 g, 69%). $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 0.87 (m, 18H, CH$_3$), 1.26 (m, 12 H, CH$_2$), 1.72 (m, 12 H, CH$_2$), 2.14 (s, 3H, CH$_3$), 3.93 (m, 12H, OCH$_2$), 5.41 (s, 2H, OCH$_2$), 7.09 (s, 4H, H arom.), 7.29 (m, 2 H, CH), 7.81 (m, 2 H, CH), 8.09 (s, 2H, CH), 8.37 (s, 2H, CH), 8.56 (m, 6H, CH + NH). $^{13}$C{$^1$H} DEPT NMR (75.47 MHz, CDCl$_3$) 14.03 (CH$_3$), 14.09 (CH$_3$), 22.67 (CH$_2$), 22.70 (CH$_2$), 26.08 (CH$_2$), 28.92 (CH$_2$), 29.29 (CH$_2$), 29.34 (CH$_2$), 29.39 (CH$_2$), 29.54 (CH$_2$), 30.34 (CH$_2$), 30.41 (CH$_2$), 31.83 (CH$_2$), 31.91 (CH$_2$), 65.21 (OCH$_2$), 69.16 (OCH$_2$), 73.46 (OCH$_2$), 105.97 (CH), 119.14 (CH), 121.45 (CH), 123.92 (CH), 124.47 (CH), 136.84 (CH), 148.91 (CH), 127.69 (Cq), 128.85 (Cq), 134.15 (Cq), 136.87 (Cq), 141.41 (Cq), 146.97 (Cq), 153.07 (Cq), 155.60 (Cq), 155.77 (Cq), 165.19 (C=O), 166.41 (C=O). UV-vis (CH$_2$Cl$_2$, 23 °C): $\lambda_{max}$ ($\epsilon$, M$^{-1}$cm$^{-1}$) = 274 (103900), 252 (98400). IR (KBr): 3437 (vNH), 3208 (vNH), 2924 (vCH), 2854 (vCH), 1727 (vCOO), 1637 (vCO), 1618 (vCO), 1584 (vC=C, vC=N), 1517 ($\delta$NH), 1490, 1467, 1428, 1408, 1384, 1337, 1264, 1214, 1190, 1114, 1072, 1039 cm$^{-1}$. MS (FAB+, mNBA): $m/z$ (%) = 2061.2 (100) [M+H]$^+$. Anal. Calcd for C$_{134}$H$_{221}$N$_5$O$_{10}$: C, 78.04; H, 10.80; N, 3.40; Found C, 77.89; H, 10.43; N, 3.27.
Figure S1. Differential Scanning Calorimetry (DSC) curve of the T12-ester compound (top: second heating curve; bottom: first cooling curve).

Figure S2. Differential Scanning Calorimetry (DSC) curve of the T12-ethynyl compound (Top: first heating curve; bottom: first cooling curve).
Figure S3. XRD pattern of the T\textsuperscript{12} ester compound at 180 °C.

References


